DYSTAR TEXTILFARBEN GMBH & CO. DEUTSCHLAND KG 2003/C 004 Dr. My

Description

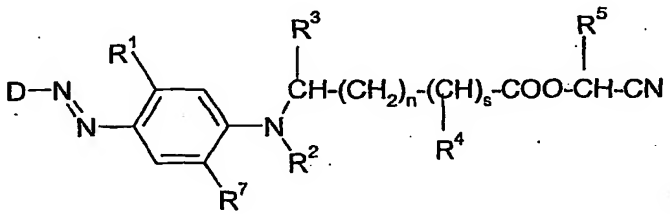
Disperse Azo Dyestuffs

The present invention relates to the field of disperse dyes.

Disperse dyestuffs containing cyanomethyl ester groups are known from literature and are described for example in GB 909,843, DE-A 2130992, GB 1,457,532, GB 1,536,429, FR-A 1,531,147, US 3,776,898, JP 55161857, GB 2,104,088, EP 0 685 531 A1 and WO 95/20014.

The inventor of the present invention has surprisingly found that dyeings on polyester with very good wet fastness properties can be obtained if selected dyestuffs containing one cyanomethylester group as defined below are used.

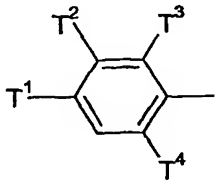
The present invention claims dyestuffs of the formula I



(I)

wherein

D is a group of the formula (IIa)



(IIa)

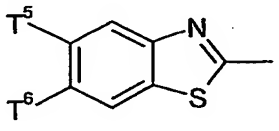
wherein

T^1, T^2 and T^3 are, independently, hydrogen, halogen or nitro;

T^4 is hydrogen, halogen, cyano or nitro;

wherein at least one of T^1, T^2, T^3 and T^4 is not hydrogen;

or a group of the formula (IIb)



(IIb)

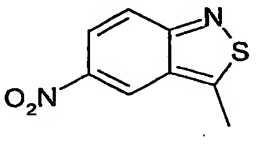
wherein

T^5 is hydrogen or halogen; and

T^6 is hydrogen $-SO_2CH_3$, -SCN or nitro;

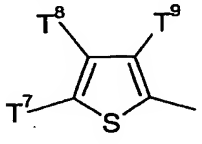
wherein at least one of T^5 and T^6 is not hydrogen;

or a group of the formula (IIc)



(IIc)

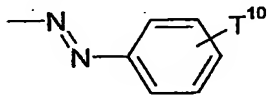
or a group of the formula (IId)



(IId)

wherein

T^7 is nitro, –CHO or a group of the formula

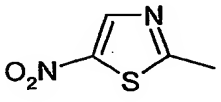


wherein T^{10} is –H, halogen, nitro and cyano;

T^8 is hydrogen or halogen; and

T^9 is nitro, cyano, $-COCH_3$ or $-COOT^{10}$, wherein T^{10} is (C_1-C_4)-alkyl;

or a group of the formula (IIe)



(IIe)

R^1 is hydrogen, (C_1-C_4)-alkyl or $-NCOR^6$, where R^6 is (C_1-C_4)-alkyl or phenyl;

R^2 is unsubstituted (C_1-C_6)-alkyl, substituted (C_1-C_6)-alkyl, benzyl or phenylethyl;

R^3 is hydrogen or methyl;

R^4 is hydrogen or methyl;

R^5 is hydrogen, methyl or phenyl;

R^7 is hydrogen, chloro, methoxy or ethoxy;

n is 0, 1 or 2;

s is 0 or 1;

with the proviso that

in the case R^1, R^3, R^4, R^5 and R^7 are hydrogen and $n = 0$

D is a group of the formula (IIc), (IId), (IIe) or (IIa) wherein T^1 is not nitro

- if T^2, T^3 and T^4 are hydrogen,
- if T^2 and T^3 are hydrogen and T^4 is chlorine or cyano and
- if T^2 and T^4 are hydrogen and T^3 is chlorine; and

with the further proviso that

R^2 is unsubstituted (C_1-C_6)-alkyl if R^1 is methyl, R^3, R^4, R^5 and R^7 are hydrogen and $n = 0$.

Alkyl groups standing for R^1, R^6 or T^{10} may be straight-chain or branched and are preferably methyl, ethyl, n-propyl, i-propyl or n-butyl. The same applies to alkyl groups standing for R^2, which can in addition be pentyl or hexyl. Substituted alkyl groups standing for R^2 are preferably substituted by hydroxyl, (C_1-C_4)-alkoxy or halogen.

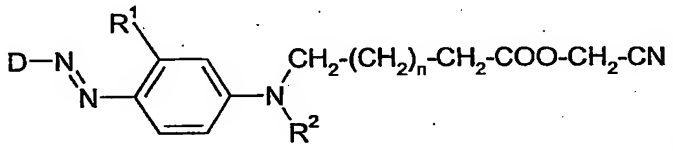
Halogen standing for T^1, T^2, T^3, T^4, T^5 or T^8 are preferably chlorine or bromine.

Preferred examples for D derive from the following amines:

2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2-chloro-4-nitroaniline, 4-chloro-2-nitroaniline, 2-bromo-4-nitroaniline, 2,6-dichloro-4-nitroaniline, 2,6-dibromo-4-nitroaniline, 2-chloro-6-bromo-4-nitroaniline, 2,5-dichloro-4-nitroaniline, 2-cyano-4-nitroaniline, 2-cyano-6-bromo-4-nitroaniline, 2-cyano-6-chloro-4-nitroaniline, 2,4-dinitroaniline, 2-chloro-4,6-dinitroaniline, 2-bromo-4,6-dinitroaniline, 2,6-dicyano-4-nitroaniline, 2-cyano-4,6-dinitroaniline, 2-amino-5-nitrothiazole, 2-amino-3,5-dinitrothiophene, 2-amino-3-ethoxycarbonyl-5-nitrothiophene, 2-amino-3-acetyl-5-nitrothiophene, 2-amino-3-cyano-5-nitrothiophene, 2-amino-3-

cyano-4-chloro-5-formylthiophene, 7-amino-5-nitrobenzoisothiazole, 2-amino-6-nitrobenzothiazole, 2-amino-6-methylsulphonylbenzothiazole; 2-amino-6-thiocyanatobenzothiazole, 2-amino-5,6-dichlorobenzothiazole and 2-amino-6,7-dichlorobenzothiazole (mixture).

Preferred disperse dyestuffs according to the present invention are of the general formula (Ia)



(Ia)

wherein

D is a group of the formulae (IIa), (IIb), (IIc), (IId) or (IIe);

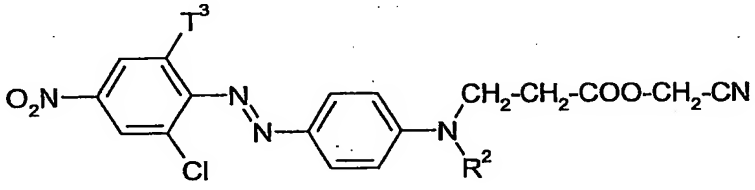
R^1 is $(C_1$-$C_4)$-alkyl;

R^2 is unsubstituted $(C_1$-$C_6)$-alkyl, benzyl or phenylethyl; and

n is 0, 1 or 2.

In especially preferred dyestuffs of formula (Ia) R^1 is methyl, R^2 is ethyl and n is 0.

Other preferred disperse dyestuffs according to the present invention are of the general formula (Ib)



(Ib)

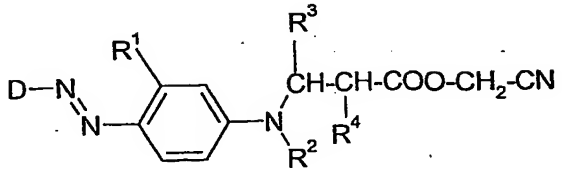
wherein

T^3 is bromo or chloro; and

R^2 is unsubstituted $(C_1$-$C_6)$-alkyl, substituted $(C_1$-$C_6)$-alkyl, benzyl or phenylethyl;

In especially preferred dyestuffs of formula (Ib) R^2 is ethyl, benzyl or phenethyl.

Still other preferred disperse dyestuffs according to the present invention are of the general formula (Ic)



(Ic)

wherein

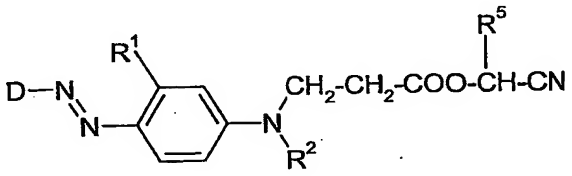
D is a group of the formulae (IIa), (IIb), (IIc), (IId) or (IIe);

R^1 is hydrogen, $(C_1$-$C_4)$-alkyl or $-NCOR^6$, where R^6 is $(C_1$-$C_4)$-alkyl or phenyl;

R^2 is unsubstituted $(C_1$-$C_6)$-alkyl, substituted $(C_1$-$C_6)$-alkyl, benzyl or phenylethyl; and

R^3 is hydrogen and R^4 is methyl or R^3 is methyl and R^4 is hydrogen.

Still other preferred disperse dyestuffs according to the present invention are of the general formula (Id)



wherein

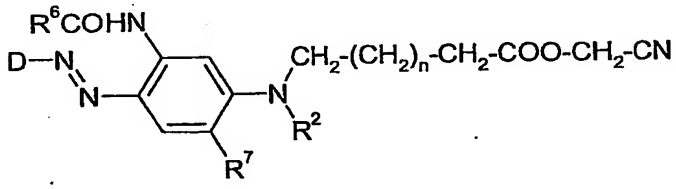
D is a group of the formulae (IIa), (IIb), (IIc), (IId) or (IIe);

R^1 is hydrogen, $(C_1$-$C_4)$-alkyl or $-NCOR^6$, where R^6 is $(C_1$-$C_4)$-alkyl or phenyl;

R^2 is unsubstituted $(C_1$-$C_6)$-alkyl, substituted $(C_1$-$C_6)$-alkyl, benzyl or phenylethyl; and

R^5 is methyl or phenyl;

Still other preferred disperse dyestuffs according to the present invention are of the general formula (Ie)



(Ie)

wherein

D is a group of the formulae (IIa), (IIb), (IIc), (IId) or (IIe);

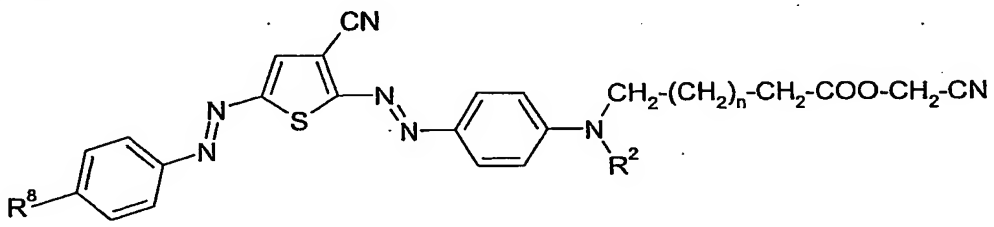
R^2 is unsubstituted (C_1-C_6)-alkyl, substituted (C_1-C_6)-alkyl, benzyl or phenylethyl;

R^6 is (C_1-C_4)-alkyl or phenyl;

R^7 is chloro, methoxy or ethoxy; and

n is 0, 1 or 2.

Still other preferred disperse dyestuffs according to the present invention are of the general formula (If)



(If)

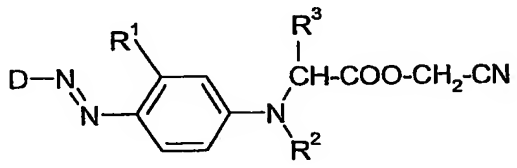
wherein

R^2 is unsubstituted (C_1-C_6)-alkyl, substituted (C_1-C_6)-alkyl, benzyl or phenylethyl;

R^8 is nitro; and

n is 0, 1 or 2;

Still other preferred disperse dyestuffs according to the present invention are of the general formula (Ig)



(Ig)

wherein

D is a group of the formulae (IIa), (IIb), (IIc), (IId) or (IIe);

R^1 is hydrogen, (C_1-C_4)-alkyl or $-NCOR^6$, where R^6 is (C_1-C_4)-alkyl or phenyl;

R^2 is unsubstituted (C_1-C_6)-alkyl, substituted (C_1-C_6)-alkyl, benzyl or phenylethyl; and

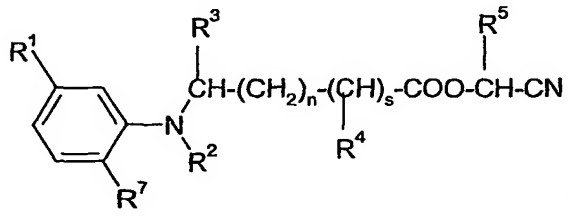
R^3 is hydrogen or methyl.

The compounds of the formula I may be obtained by usual methods for the preparation of azo compounds such as by diazotisation of an amine of the formula III

$$D\text{-}NH_2 \qquad (III)$$

wherein D is defined as given above,

and coupling onto a compound of the formula IV



(IV)

wherein R^1, R^2, R^3, R^4, R^5 and R^7 are defined as given above.

Typically the amine of the formula (III) may be diazotised in an acidic medium, such as acetic, propionic or hydrochloric acid using a nitrosating agent such as nitrosylsulphuric acid, sodium nitrite or methylnitrite at a temperature from -10°C to 10°C. Coupling onto the compound of the formula (IV) may be achieved by adding the diazotised amine to the compound of the formula (IV) under conditions described in literature and known to the skilled persons.
After coupling the compound of the formula (I) may be recovered from the reaction mixture by any convenient means such as filtration.
The compounds of the formulae (III) and (IV) are known and can be obtained by methods described in literature or known to the skilled person.

The compounds of the formula (I) are useful for dyeing and printing of synthetic textile material particularly polyester textile materials and fibre blends thereof with for example cellulosic materials like cotton, to which they impart colours which have excellent wet fastness properties.

Dyeing of the fibre goods mentioned with the dyestuffs of the formula (I) can be carried out in a manner known per se, preferably from aqueous dispersions, if appropriate in the presence of carriers, at between 80 and 110°C, by the exhaust process or by the HT process in a dyeing autoclave at 110 to 140°C,

and by the so-called thermofixing process, in which the goods are padded with the dye liquor and then fixed at about 180 to 230°C.

The fibre goods mentioned can as well be printed in a manner known pers e by a procedure in which the dyestuffs of the formula (I) are incorporated into a printing paste and the goods printed with the paste are treated , if appropriate in the presence of a carrier, with HT steam, pressurized steam or dry heat at temperatures between 180 and 230°C to fix the dyestuff.

The dyestuffs of the formula (I) should be present in the finest possible dispersion in the dye liquors and printing pastes employed in the above applications.

The fine dispersion of the dyestuffs is effected in a manner known per se by a procedure in which the dyestuff obtained during preparation is suspended ina liquid medium, preferably in water, together with dispersing agents and the mixture is exposed to the action of shearing forces, the particles originally present being comminuted mechanically to the extent that an optimum specific surface area is achieved and sedimentation of the dyestuff is as low as possible. The particle size of the dyestuffs is in general between 0.5 and 5 m, preferably about 1 m.

The dispersing agents used can be nonionic or anionic. Nononic dispersing agents are, for example, reaction products of alkylene oxides, such as, for example, ethylene oxide or propylene oxide, with alkylatable compounds, such as for example fatty alcohols, fatty amines, fatty acids, phenols, alkylphenols and carboxylic acid amines. Anionic dispersing agnets are, for example, lignin-sulphonates, alkyl- or alkylarylsulphonates or alkylaryl polyglycol ethersulphates.

For most methods of use, the dyestuff formulations thus obtained should be pourable. The dyestuff and dispersing agent content is therefore limited in these cases. In general, the dispersions are brought to a dyestuff content of up to 50 per cent by weight and a dispersing agent content of up to 25 per cent by weight. For economic reasons, the dyestuff contents usually do not fall below 15 per cent by weight.

The dispersions can also comprise other auxiliaries, for example those which act

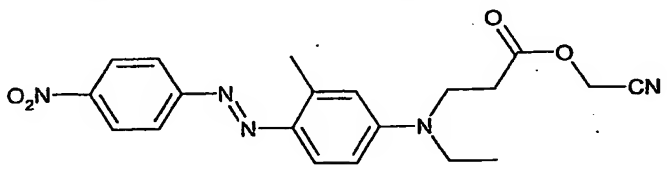
as oxidizing agents or fungicidal agents. Such agents are well known in the art. The dyestuff dispersion thus obtained can be used very advantageously for the preparation of printing pastes and dye liquors.

For certain fields of use, powder formulations are preferred. These powders comprise the dyestuff, dispersing agents and other auxiliaries, such as, for example, wetting agents, oxidizing agents, preservatives and dust removal agents.

A preferred preparation process for pulverulent dyestuff formulations comprises removing the liquid from the liquid dyestuff dispersions described above, for example by vacuum drying, freeze drying, by drying on roller dryers, but preferably by spray drying.

Example 1

4-(4-nitrophenylazo)-3-methyl-N-ethyl-N-(2-cyanomethoxy- carbonylethyl) aniline

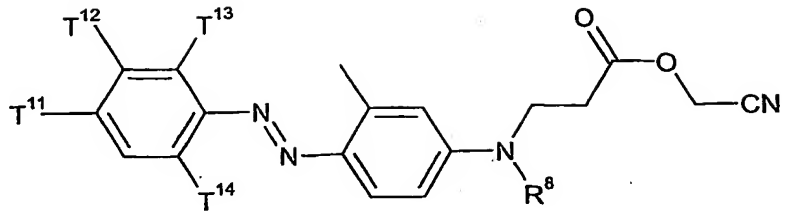


4-nitroaniline (4.1parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (50parts). Nitrosyl sulphuric acid 40% (11.4parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution obtained was added gradually to a stirred coupling mixture of N-ethyl, N-(2-cyanomethoxycarbonylethyl)-m-toluidine (7.3parts), methanol (50parts), water (200parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(4-nitrophenylazo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline (6.5parts) λmax = 486nm (acetone)

When applied to polyester materials from aqueous dispersion, red shades with excellent wet and light fastness properties were seen.

The following examples of dyes of formula (Iaa):



(Iaa)

were prepared by the procedure of Example1 (see Table 1)

Table 1

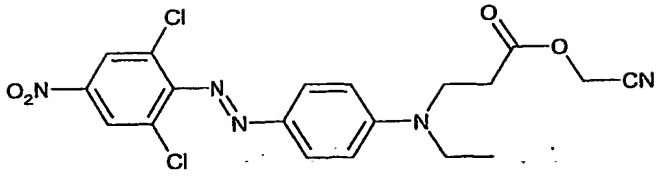
Example	T^{11}	T^{12}	T^{13}	T^{14}	R^8	λmax (nm)
2	-H	-H	$-NO_2$	-H	$-C_2H_5$	479
3	-H	$-NO_2$	-H	-H	$-C_2H_5$	468
4	$-NO_2$	-H	-Cl	-H	$-C_2H_5$	508
5	-Cl	-H	$-NO_2$	-H	$-C_2H_5$	501
6	$-NO_2$	-H	-Br	-H	$-C_2H_5$	507
7	$-NO_2$	-H	-Cl	-Cl	$-C_2H_5$	450
8	$-NO_2$	-H	-Br	-Br	$-C_2H_5$	449
9	$-NO_2$	-H	-Cl	-Br	$-C_2H_5$	449
10	$-NO_2$	-Cl	-H	-Cl	$-C_2H_5$	518
11	$-NO_2$	-H	-CN	-H	$-C_2H_5$	534
12	$-NO_2$	-H	-CN	-Br	$-C_2H_5$	544
13	$-NO_2$	-H	-CN	-Cl	$-C_2H_5$	545
14	$-NO_2$	-H	$-NO_2$	-H	$-C_2H_5$	535
15	$-NO_2$	-H	-Br	$-NO_2$	$-C_2H_5$	542
16	$-NO_2$	-H	-Cl	$-NO_2$	$-C_2H_5$	544
17	$-NO_2$	-H	-CN	-CN	$-C_2H_5$	582
18	$-NO_2$	-H	-CN	$-NO_2$	$-C_2H_5$	590
19	$-NO_2$	-H	-H	-H	$-C_4H_9$	490

Example	T^{11}	T^{12}	T^{13}	T^{14}	R^8	λmax (nm)
20	$-NO_2$	-H	-Cl	-H	$-C_4H_9$	513
21	$-NO_2$	-H	-Cl	-Cl	$-C_4H_9$	453
22	$-NO_2$	-H	-Cl	-Br	$-C_4H_9$	453
23	$-NO_2$	-H	-Br	-Br	$-C_4H_9$	452
24	$-NO_2$	-H	-CN	-H	$-C_4H_9$	539
25	$-NO_2$	-H	$-NO_2$	-H	$-C_4H_9$	540
26	$-NO_2$	-H	-CN	-Br	$-C_4H_9$	549
27	$-NO_2$	-H	-CN	-Cl	$-C_4H_9$	548
28	$-NO_2$	-H	-Br	$-NO_2$	$-C_4H_9$	548
29	$-NO_2$	-H	-Cl	$-NO_2$	$-C_4H_9$	549
30	-H	-H	$-NO_2$	-H	$-C_4H_9$	483
31	$-NO_2$	-H	-CN	-CN	$-C_4H_9$	586
32	$-NO_2$	-H	-H	-H	$-CH_2[C_6H_5]$	479
33	$-NO_2$	-H	$-NO_2$	-H	$-CH_2[C_6H_5]$	530
34	-H	-H	$-NO_2$	-H	$-CH_2[C_6H_5]$	470
35	-H	$-NO_2$	-H	-H	$-CH_2[C_6H_5]$	460
36	$-NO_2$	-H	-Cl	-H	$-CH_2[C_6H_5]$	498
37	$-NO_2$	-H	-Cl	-Cl	$-CH_2[C_6H_5]$	446
38	$-NO_2$	-H	-Br	-Br	$-CH_2[C_6H_5]$	445
39	$-NO_2$	-H	-Br	-Cl	$-CH_2[C_6H_5]$	444
40	$-NO_2$	-H	-CN	-H	$-CH_2[C_6H_5]$	528
41	$-NO_2$	-H	-CN	-Br	$-CH_2[C_6H_5]$	539
42	$-NO_2$	-H	-CN	-Cl	$-CH_2[C_6H_5]$	539
43	$-NO_2$	-H	-Br	$-NO_2$	$-CH_2[C_6H_5]$	538
44	$-NO_2$	-H	-Cl	$-NO_2$	$-CH_2[C_6H_5]$	537

Example	T^{11}	T^{12}	T^{13}	T^{14}	R^8	λmax (nm)
45	$-NO_2$	-H	-CN	$-NO_2$	$-CH_2[C_6H_5]$	580
46	$-NO_2$	-H	-CN	-CN	$-CH_2[C_6H_5]$	577
47	$-NO_2$	-H	-H	-H	$-C_3H_7$	487
48	$-NO_2$	-H	-Cl	-H	$-C_3H_7$	509
49	$-NO_2$	-H	-Cl	-Cl	$-C_3H_7$	452
50	$-NO_2$	-H	-Cl	-Br	$-C_3H_7$	451
51	$-NO_2$	-H	-Br	-Br	$-C_3H_7$	452
52	$-NO_2$	-H	-CN	-H	$-C_3H_7$	536
53	$-NO_2$	-H	$-NO_2$	-H	$-C_3H_7$	537
54	$-NO_2$	-H	-CN	-Br	$-C_3H_7$	546
55	$-NO_2$	-H	-CN	-Cl	$-C_3H_7$	548
56	$-NO_2$	-H	-Br	$-NO_2$	$-C_3H_7$	544
57	$-NO_2$	-H	-Cl	$-NO_2$	$-C_3H_7$	545
58	-H	-H	$-NO_2$	-H	$-C_3H_7$	480
59	$-NO_2$	-H	-CN	-CN	$-C_3H_7$	584
60	$-NO_2$	-H	-Cl	-H	$-CH_3$	504
61	$-NO_2$	-H	-CN	-H	$-CH_3$	529
62	$-NO_2$	-H	-Cl	-CN	$-CH_3$	543
63	$-NO_2$	-H	-Br	-CN	$-CH_3$	542
64	$-NO_2$	-H	-Br	$-NO_2$	$-CH_3$	539

Example 65

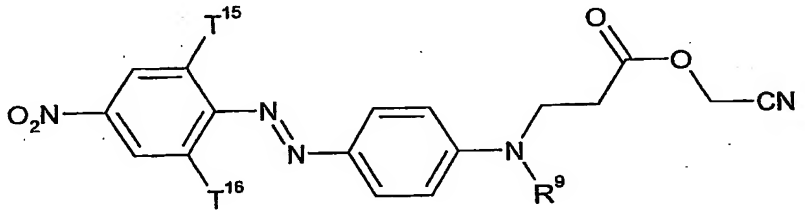
4-(2,6-dichloro-4-nitrophenylazo)-N-ethyl-N-(2-cyanomethoxy- carbonylethyl) aniline



2,6-dichloro-4-nitroaniline (6.2parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (11.4parts) was added below 5°C and the mixture was stirred for 30 minutes. The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-2(cyanomethoxycarbonylethyl)-aniline (8.3parts), methanol (50parts), water (300parts) and sulphamic acid (1part). After one hour the product was isolated by filtration, washed with cold water and dried to yield, 4-(2,6-dichloro-4-nitrophenylazo)-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline (9.5parts) λmax = 432nm (acetone)

When applied to polyester materials from aqueous dispersion, yellow brown shades with excellent wet and light fastness properties were seen.

The following examples of dyes of Formula (Iba)



(Iba)

were prepared by the procedure of Example 65 (see Table 2)

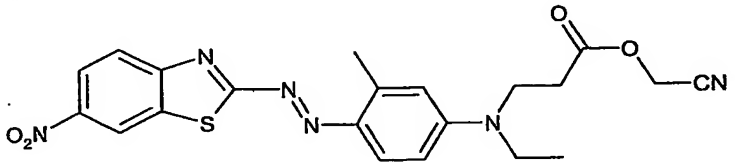
Table 2

Example	T^{15}	T^{16}	R^9	λmax (nm)
66	-Cl	-Cl	$-C_3H_7$	433
67	-Cl	-Cl	$-C_4H_9$	434

Example	T^{15}	T^{16}	R^9	λmax (nm)
68	-Cl	-Cl	$-CH_2[C_6H_5]$	420
69	-Cl	-Cl	$-CH_3$	425
70	-Cl	-Br	$-C_2H_5$	430
71	-Cl	-Br	$-C_3H_7$	431
72	-Cl	-Br	$-C_4H_9$	433
73	-Cl	-Br	$-CH_2[C_6H_5]$	420
74	-Cl	-Br	$-CH_3$	424
75	-Br	-Br	$-C_2H_5$	430
76	-Br	-Br	$-C_3H_7$	432
77	-Br	-Br	$-C_4H_9$	431
78	-Br	-Br	$-CH_2[C_6H_5]$	421
79	-Br	-Br	$-CH_3$	424

Example 80

4-(6-nitrobenzothiazol-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline



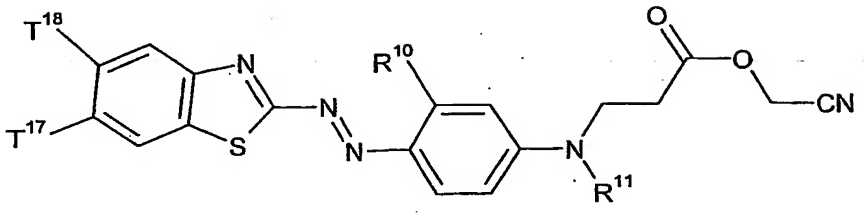
2-amino-6-nitrobenzothiazole (3.9parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (7.6parts) was added below 5°C and the mixture was stirred for 1 hour. The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(2-cyanomethoxycarbonylethyl)-m-toluidine (5.9parts), methanol (25parts), water (200parts) and sulphamic acid (0.5parts). After one hour the product was isolated by filtration, washed with cold water and dried to yield,

4-(6-nitrobenzothiazol-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonyl ethyl) aniline (2.4parts) λmax = 545nm (acetone)

When applied to polyester materials from aqueous dispersion, rubine shades with excellent wet and light fastness properties were seen.

5

The following examples of dyes of Formula (Iab):



(Iab)

were prepared by the procedure of Example 80 (see Table 3)

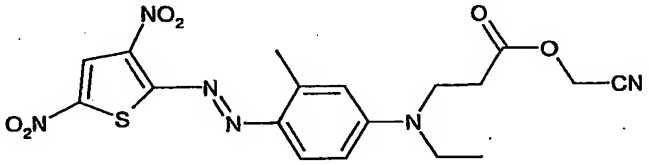
Table 3

Example	T^{17}	T^{18}	R^{10}	R^{11}	λmax nm
81	$-SO_2CH_3$	-H	$-CH_3$	$-CH_3$	527
82	$-NO_2$	-H	$-CH_3$	$-CH_3$	543
83	$-NO_2$	-H	$-CH_3$	$-C_3H_7$	545
84	$-NO_2$	-H	$-CH_3$	$-C_4H_9$	548
85	$-NO_2$	-H	$-CH_3$	$-CH_2[C_6H_5]$	538
86	-Cl	-Cl	$-CH_3$	$-C_2H_5$	526
87	-Cl	-Cl	$-CH_3$	$-CH_3$	522
88	-Cl	-Cl	$-CH_3$	$-C_3H_7$	528
89	-Cl	-Cl	$-CH_3$	$-C_4H_9$	530
90	-Cl	-Cl	$-CH_3$	$-CH_2[C_6H_5]$	521
91	$-SO_2CH_3$	-H	$-CH_3$	$-C_3H_7$	531
92	$-SO_2CH_3$	-H	$-CH_3$	$-C_4H_9$	533
93	$-SO_2CH_3$	-H	$-CH_3$	$-CH_2[C_6H_5]$	525
94	-SCN	-H	$-CH_3$	$-C_2H_5$	534
95	-SCN	-H	$-CH_3$	$-CH_3$	530
96	-SCN	-H	$-CH_3$	$-C_3H_7$	535

Example	T^{17}	T^{18}	R^{10}	R^{11}	λmax nm
97	-SCN	-H	$-CH_3$	$-C_4H_9$	537
98	-SCN	-H	$-CH_3$	$-CH_2[C_6H_5]$	529
99	$-NO_2$	-H	-H	$-C_4H_9$	535
100	$-NO_2$	-H	-H	$-CH_2[C_6H_5]$	525
101	-SCN	-H	-H	$-C_4H_9$	523
102	-SCN	-H	-H	$-CH_2[C_6H_5]$	516
103	-Cl	-Cl	-H	$-C_4H_9$	519
104	-Cl	-Cl	-H	$-CH_2[C_6H_5]$	509
105	$-SO_2CH_3$	-H	-H	$-C_4H_9$	521
106	$-SO_2CH_3$	-H	-H	$-CH_2[C_6H_5]$	512

Example 107

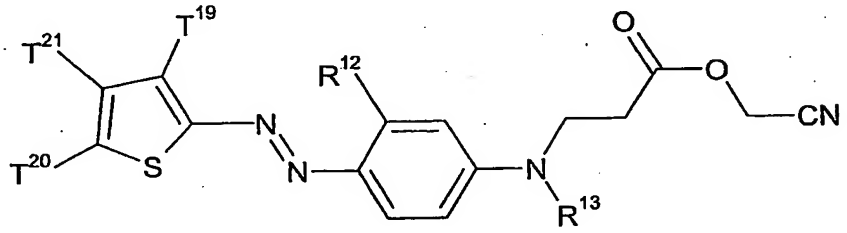
4-(3,5-dinitrothiophen-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline



2-amino-3,5-dinitrothiophene (3.1parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (50parts). Nitrosyl sulphuric acid 40% (5.7parts) was added below 5°C and the mixture was stirred for 30 mins. The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(2-cyanomethoxycarbonyethyl)-m-toluidine (4.0parts), acetone (50parts), water (300parts) and sulphamic acid (0.5parts). After one hour the product was isolated by filtration, washed with cold water and dried to yield, 4-(3,5-dinitrothiophen-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonyl- ethyl) aniline (3.0parts) λmax = 640nm (acetone)

When applied to polyester materials from aqueous dispersion, blue shades with excellent wet and light fastness properties were seen.

The following examples of dyes of Formula (Iac):



(Iac)

were prepared by the procedure of Example 107 (see Table 4)

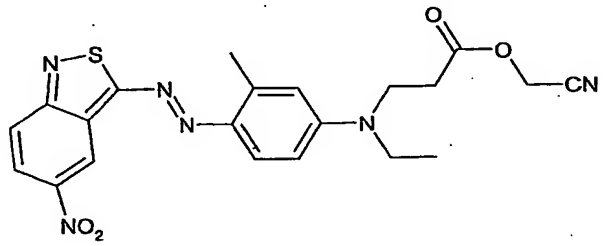
Table 4

Example	T^{19}	T^{20}	T^{21}	R^{12}	R^{13}	λmax (nm)
108	$-NO_2$	$-NO_2$	-H	-H	$-C_2H_5$	620
109	$-NO_2$	$-NO_2$	-H	-H	$-C_4H_9$	625
110	$-NO_2$	$-NO_2$	-H	-H	$-C_3H_7$	622
111	$-NO_2$	$-NO_2$	-H	-H	$-CH_2[C_6H_5]$	611
112	$-NO_2$	$-NO_2$	-H	$-CH_3$	$-C_4H_9$	645
113	$-NO_2$	$-NO_2$	-H	$-CH_3$	$-C_3H_7$	640
114	$-NO_2$	$-NO_2$	-H	$-CH_3$	$-CH_2[C_6H_5]$	632
115	$-COOC_2H_5$	$-NO_2$	-H	$-CH_3$	$-C_2H_5$	595
116	$-COOC_2H_5$	$-NO_2$	-H	-H	$-C_4H_9$	583
117	$-COCH_3$	$-NO_2$	-H	$-CH_3$	$-C_2H_5$	599
118	$-COCH_3$	$-NO_2$	-H	$-CH_3$	$-C_4H_9$	603
119	$-COCH_3$	$-NO_2$	-H	-H	$-C_4H_9$	585
120	-CN	$-NO_2$	-H	$-CH_3$	$-C_2H_5$	604
121	-CN	$-NO_2$	-H	$-CH_3$	$-CH_2[C_6H_5]$	595
122	-CN	-CHO	-Cl	$-CH_3$	$-C_2H_5$	585

Example	T^{19}	T^{20}	T^{21}	R^{12}	R^{13}	λmax (nm)
123	-CN	-CHO	-Cl	$-CH_3$	$-C_4H_9$	591
124	-CN	-CHO	-Cl	-H	$-C_4H_9$	579
125	$-COOC_2H_5$	$-NO_2$	-H	-H	$-CH_2[C_6H_5]$	565
126	$-COOC_2H_5$	$-NO_2$	-H	$-CH_3$	$-C_4H_9$	601

Example 127

4-(5-nitrobenzisothiazol-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline

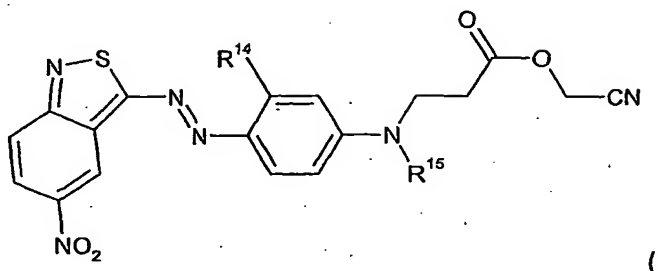


7-amino-5-nitrobenzoisothiazole (2.9parts) was added to a mixture of sulphuric acid 98% (15parts) and phosphoric acid (4parts) stirring at room temperature. The mixture was heated to 55°C and was stirred at that temperature for 30mins. Nitrosyl sulphuric acid 40% (6.1parts) was added below 5°C and the mixture was stirred for 2hrs.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(2-cyanomethoxycarbonylethyl)-m-toluidine (4.8parts), acetone (50parts), water (100parts) and sulphamic acid (0.5parts). Sodium acetate was added to increase the pH to 4.0 and the mixture was stirred for 1 hour. The product was isolated by filtration, washed with cold water and dried to yield, 4-(5-nitrobenzisothiazol-yl-azo)-3-methyl-N-ethyl-N-(2-cyanomethoxycarbonylethyl) aniline (2.4parts) λmax = 601nm (acetone)

When applied to polyester materials from aqueous dispersion, blue shades with excellent wet and light fastness properties were seen.

The following examples of dyes of Formula (Iad)



(Iad)

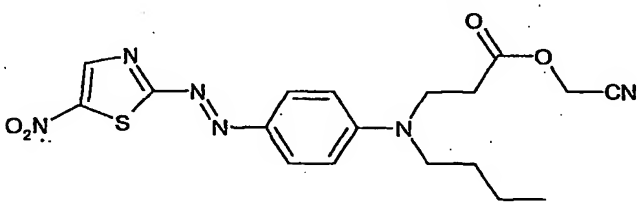
were prepared by the procedure of Example 127 (see Table 5)

Table 5

Example	R^{14}	R^{15}	λmax (nm)
128	-H	$-C_2H_5$	588
129	-H	$-CH_2[C_6H_5]$	578
130	-H	$-C_4H_9$	589
131	$-CH_3$	$-C_3H_7$	603
132	$-CH_3$	$-CH_2[C_6H_5]$	593
133	$-CH_3$	$-C_4H_9$	608

Example 134

4-(5-nitrothiazol-yl-azo)-N-butyl-N-(2-cyanomethoxy- carbonylethyl) aniline

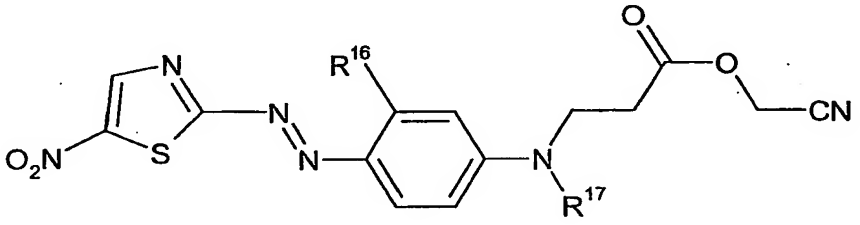


2-amino-5-nitrothiazole (2.9parts) was was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (50parts). Nitrosyl sulphuric acid 40% (7.0parts) was added below 5°C and the mixture was stirred for 30 mins. The diazo solution was added gradually to a stirred coupling mixture of N-butyl, N-2(cyanomethoxycarbonylethyl)-aniline (5.2parts), acetone (50parts), water

(200parts) and sulphamic acid (0.5parts). After one hour the product was isolated by filtration, washed with cold water and dried to yield, 4-(5-nitrothiazol-yl-azo)-N-butyl-N-(2-cyanomethoxycarbonylethyl) aniline (2.9parts) λmax = 571nm (acetone)

When applied to polyester materials from aqueous dispersion, blue shades with excellent wet and light fastness properties were seen.

The following examples of dyes of Formula (Iae)



(Iae)

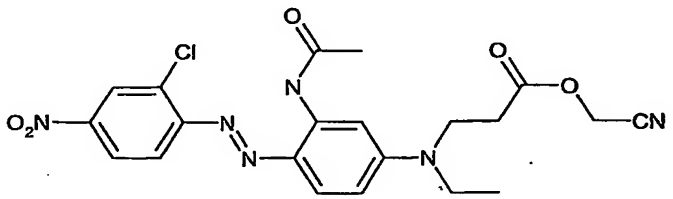
were prepared by the procedure of Example 134 (see Table 6)

Table 6

Example	R^{16}	R^{17}	λmax (nm)
135	-H	$-CH_2[C_6H_5]$	557
136	$-CH_3$	$-C_2H_5$	575
137	$-CH_3$	$-C_4H_9$	582
138	$-CH_3$	$-CH_2[C_6H_5]$	569

Example 139

4-(2-chloro-4-nitrophenylazo)-3-acetylamino-N-ethyl-N-(2-cyanomethoxycarbonylethyl)-aniline

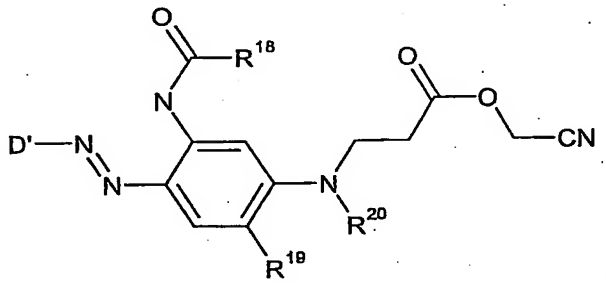


2-chloro-4-nitroaniline (3.5parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (7.0parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of 3(N-ethyl, N-cyanomethoxycarbonylethyl)-amino-acetanilide (6.3parts), methanol (40parts), water (200parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(2-chloro-4-nitrophenylazo)-3-acetylamino-N-ethyl-N-(2-cyanomethoxy-carbonylethyl)-aniline (4.1parts) λmax = 525nm (acetone)

When applied to polyester materials from aqueous dispersion, rubine shades with excellent wet and light fastness properties were seen.

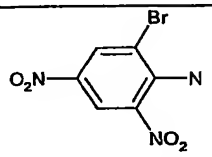
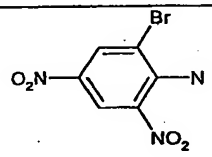
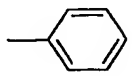
The following examples of dyes of formula (Iea):

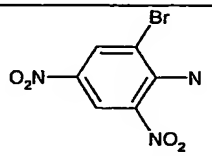
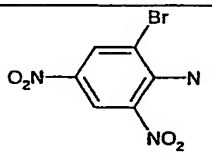
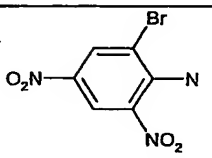
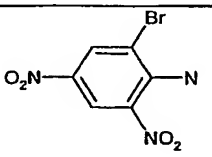
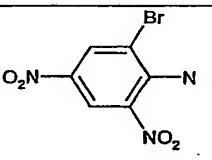
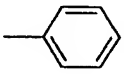
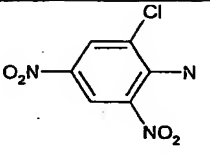
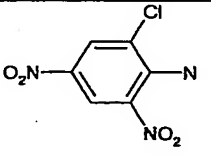
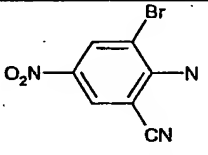
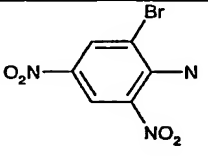


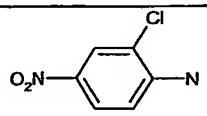
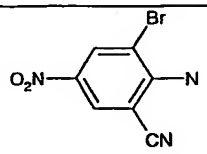
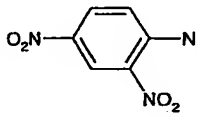
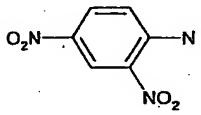
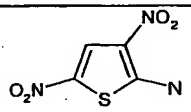
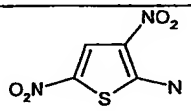
(Iea)

were prepared by the procedure of Example139 (see Table 7)

Table 7

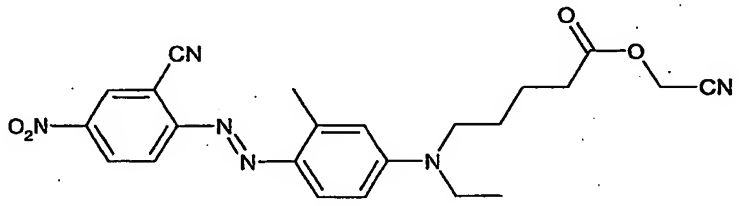
Example	D'	R^{18}	R^{19}	R^{20}	λmax (nm)
140		$-CH_3$	-H	$-C_2H_5$	550
141			-H	$-C_2H_5$	553

Example	D'	R^{18}	R^{19}	R^{20}	λmax (nm)
142		$-CH_3$	-H	$-C_4H_9$	552
143		$-C_2H_5$	-H	$-C_2H_5$	550
144		$-CH_3$	$-OCH_3$	$-C_2H_5$	596
145		$-CH_3$	$-OCH_3$	$-C_4H_9$	603
146			$-OCH_3$	-H	600
147		$-C_2H_5$	$-OCH_3$	$-C_2H_5$	596
148		$-CH_3$	-H	$-C_4H_9$	551
149		$-CH_3$	-H	$-C_2H_5$	574
150		$-C_2H_5$	-H	$-C_2H_5$	550

Example	D'	R^{18}	R^{19}	R^{20}	λmax (nm)
151		$-CH_3$	-H	$-C_4H_9$	525
152		$-CH_3$	$-OCH_3$	$-C_2H_5$	628 check
153		$-CH_3$	-H	$-C_2H_5$	539
154		$-CH_3$	$-OCH_3$	$-C_2H_5$	574
155		$-CH_3$	-H	$-C_2H_5$	634
156		$-CH_3$	$-OCH_3$	$-C_2H_5$	660

Example 157

4-(2-cyano-4-nitrophenylazo)-3-methyl-N-ethyl-N-(4-cyanomethoxycarbonylbutyl)-aniline



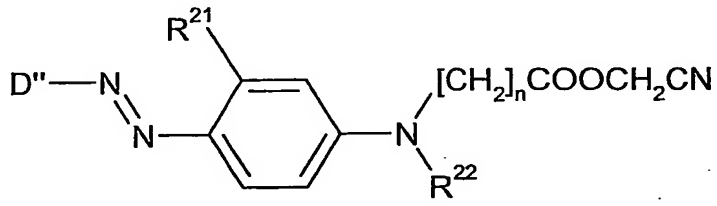
2-cyano-4-nitroaniline (3.2parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (50parts). Nitrosyl sulphuric acid 40% (7.6parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(4-cyanomethoxycarbonylbutyl)-m-toluidine (6.0parts), methanol (50parts), water (200parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(2-cyano-4-

nitrophenylazo)-3-methyl-N-ethyl-N-(4-cyanomethoxycarbonyl butyl)-aniline. (5.3parts) λmax = 548nm (acetone)

When applied to polyester materials from aqueous dispersion, rubine shades with excellent wet and light fastness properties were seen.

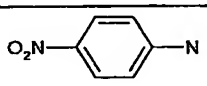
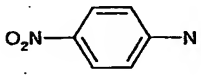
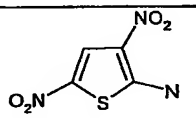
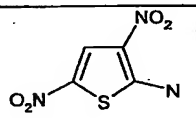
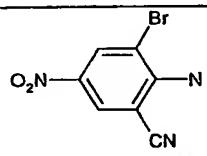
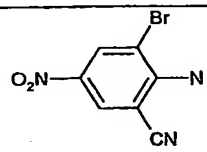
The following examples of dyes of Formula (Iaf)

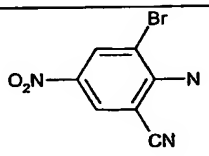
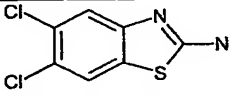
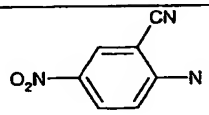
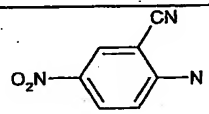
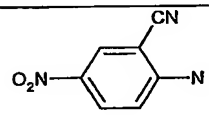


(Iaf)

were prepared by the procedure of Example157 (see Table 8)

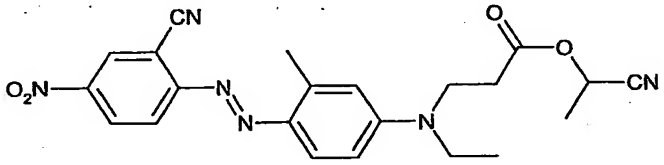
Table 8

Example	D''	R^{21}	R^{22}	n	λmax (nm)
158		-H	$-C_2H_5$	4	491
159		-H	$-C_2H_5$	3	486
160		$-CH_3$	$-C_2H_5$	4	649
161		$-CH_3$	$-C_2H_5$	3	642
162		$-CH_3$	$-C_2H_5$	4	561
163		$-CH_3$	$-C_2H_5$	3	556

Example	D''	R^{21}	R^{22}	n	λmax (nm)
164		$-CH_3$	$-C_3H_7$	3	558
165		$-CH_3$	$-C_2H_5$	4	535
166		$-CH_3$	$-C_2H_5$	4	548
167		$-CH_3$	$-C_2H_5$	3	536
168		-H	$-C_2H_5$	4	529

Example 169

4-(2-cyano-4-nitrophenylazo)-3-methyl-N-ethyl-N-(2-(1-cyanoethoxy) carbonylethyl)-aniline

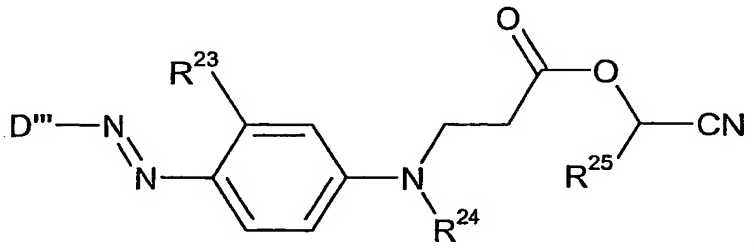


2-cyano-4-nitroaniline (2.1parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (4.9parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(2-(1-cyanoethoxy)carbonylethyl)-m-toluidine (3.7parts), acetone (50parts), water (300parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(2-cyano-4-nitrophenylazo)-3-methyl-N-ethyl-N-(2-(1-cyanoethoxy) carbonylethyl)-aniline (3.5parts) λmax = 534nm (acetone)

When applied to polyester materials from aqueous dispersion, rubine shades with excellent wet and light fastness properties were seen.

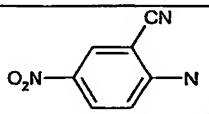
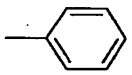
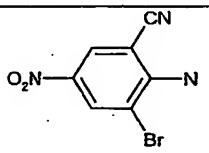
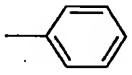
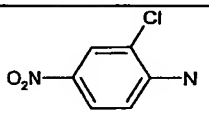
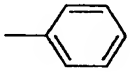
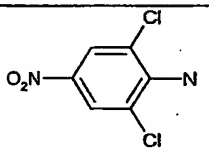
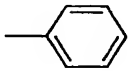
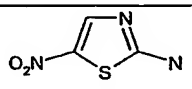
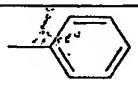
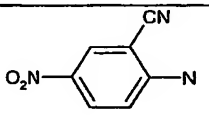
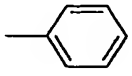
The following examples of dyes of Formula (Ida)

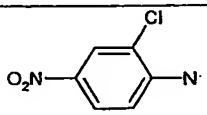
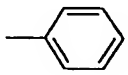
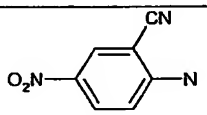
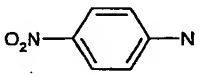
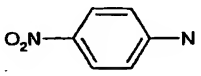
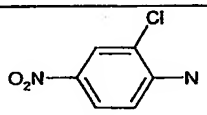
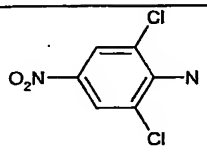
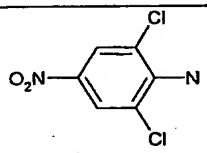
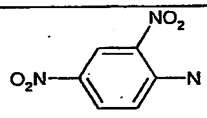
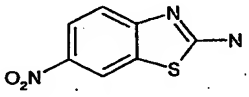
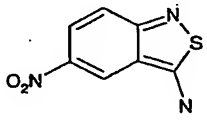
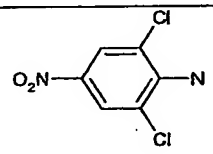


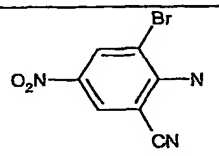
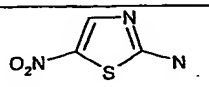
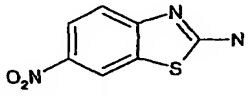
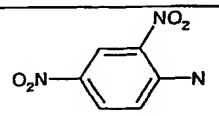
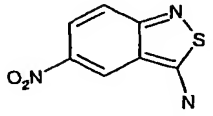
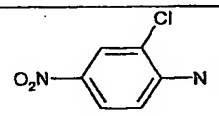
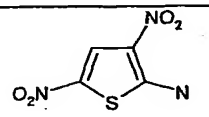
(Ida)

were prepared by the procedure of Example169 (see Table 9)

Table 9

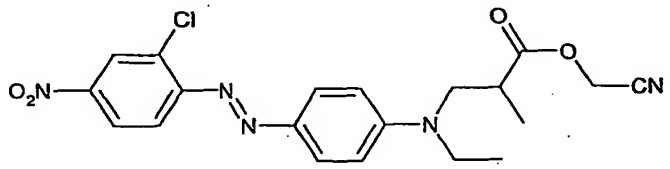
Example	D'''	R^{23}	R^{24}	R^{25}	λmax (nm)
170		$-CH_3$	$-C_2H_5$		533
171		$-CH_3$	$-C_2H_5$		544
172		$-CH_3$	$-C_2H_5$		507
173		$-CH_3$	$-C_2H_5$		446
174		$-CH_3$	$-C_2H_5$		580
175		-H	$-C_2H_5$		523

Example	D''''	R^{23}	R^{24}	R^{25}	λmax (nm)
176		-H	$-C_2H_5$		494
177		-H	$-C_2H_5$	$-CH_3$	522
178		-H	$-C_2H_5$	$-CH_3$	473
179		-H	$-C_4H_9$	$-CH_3$	480
180		-H	$-C_2H_5$	$-CH_3$	494
181		-H	$-C_2H_5$	$-CH_3$	439
182		-H	$-C_4H_9$	$-CH_3$	441
183		-H	$-C_2H_5$	$-CH_3$	521
184		-H	$-C_2H_5$	$-CH_3$	533
185		-H	$-C_2H_5$	$-CH_3$	590
186		$-CH_3$	$-C_2H_5$	$-CH_3$	449

Example	D'''	R^{23}	R^{24}	R^{25}	λmax (nm)
187		$-CH_3$	$-C_2H_5$	$-CH_3$	544
188		$-CH_3$	$-C_2H_5$	$-CH_3$	581
189		$-CH_3$	$-C_2H_5$	$-CH_3$	544
190		$-CH_3$	$-C_2H_5$	$-CH_3$	533
191		$-CH_3$	$-C_2H_5$	$-CH_3$	601
192		$-CH_3$	$-C_2H_5$	$-CH_3$	506
193		-H	$-C_2H_5$	$-CH_3$	640

Example 194

4-(2-chloro-4-nitrophenylazo)-N-ethyl-N-(2-cyanomethoxy carbonylpropyl)-aniline



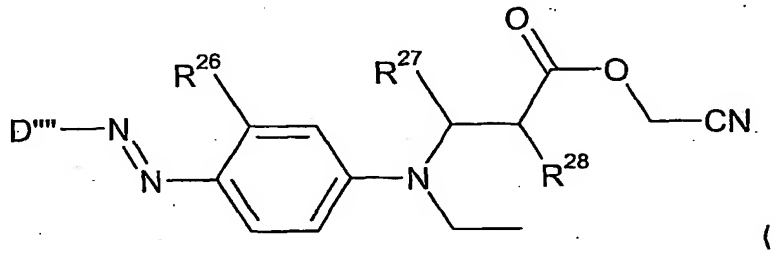
2-chloro-4-nitroaniline (parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (4.9parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-2-(cyanomethoxycarbonylpropyl)-aniline (parts), acetone (50parts), water (300parts) and sulphamic acid (1part). After two hours the product was isolated

by filtration, washed with cold water and dried to yield, 4-(2-chloro-4-nitrophenylazo)-N-ethyl-N-(2-cyanomethoxycarbonylpropyl)-aniline (3.5parts) λmax = 534nm (acetone)

When applied to polyester materials from aqueous dispersion, red shades with excellent wet and light fastness properties were seen.

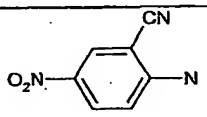
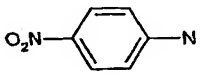
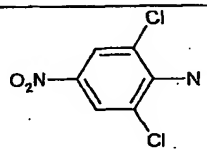
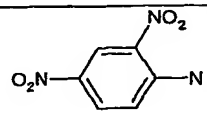
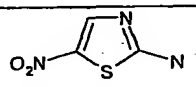
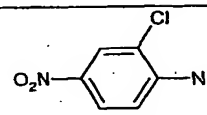
The following examples of dyes of Formula (Ica)

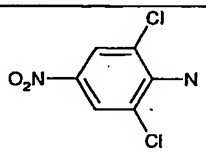
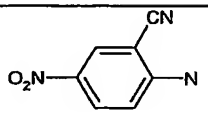
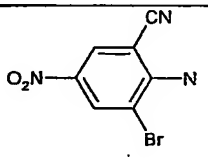
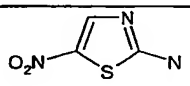
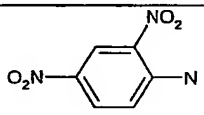
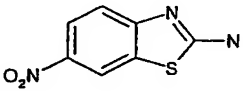
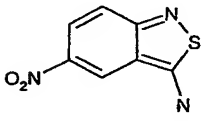
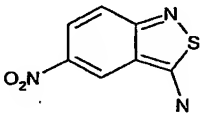
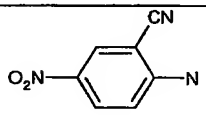
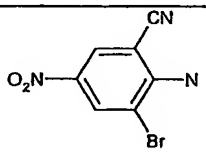
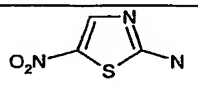
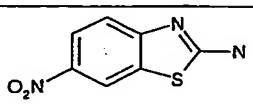


(Ica)

were prepared by the procedure of Example194 (see Table 10)

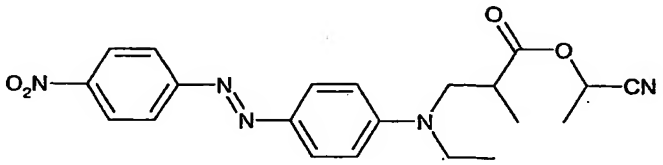
Table10

Example	D''''	R^{26}	R^{27}	R^{28}	λmax (nm)
195		-H	-H	$-CH_3$	521
196		-H	-H	$-CH_3$	473
197		-H	-H	$-CH_3$	440
198		-H	-H	$-CH_3$	521
199		-H	-H	$-CH_3$	569
200		$-CH_3$	-H	$-CH_3$	505

Example	D''''	R^{26}	R^{27}	R^{28}	λmax (nm)
201		$-CH_3$	-H	$-CH_3$	448
202		$-CH_3$	-H	$-CH_3$	532
203		$-CH_3$	-H	$-CH_3$	541
204		$-CH_3$	-H	$-CH_3$	579
205		$-CH_3$	-H	$-CH_3$	525
206		$-CH_3$	-H	$-CH_3$	541
207		$-CH_3$	-H	$-CH_3$	599
208		-H	-H	$-CH_3$	588
209		$-CH_3$	$-CH_3$	-H	535
210		$-CH_3$	$-CH_3$	-H	544
211		$-CH_3$	$-CH_3$	-H	594
212		$-CH_3$	$-CH_3$	-H	549

Example 213

4-(4-nitrophenylazo)-N-ethyl-N-(2-(1-cyanoethoxy) carbonylpropyl)-aniline



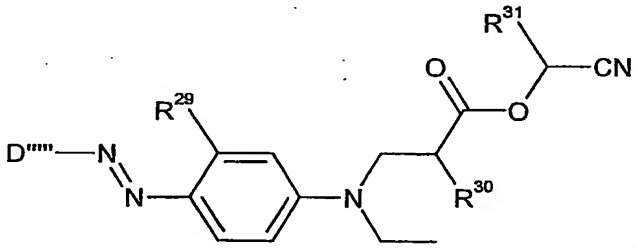
4-nitroaniline (2.0parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (50parts). Nitrosyl sulphuric acid 40% (5.7parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(2-(1-cyanoethoxy)carbonylpropyl)-aniline (4.7parts), acetone (50parts), water (200parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(4-nitrophenylazo)-N-ethyl-N-(2-(1-cyanoethoxy)carbonylpropyl)-aniline

(2.9parts) λmax = 473nm (acetone)

When applied to polyester materials from aqueous dispersion, scarlet shades with excellent wet and light fastness properties were seen.

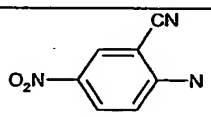
The following examples of dyes of Formula (Ih):

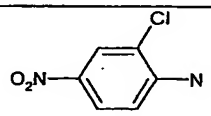
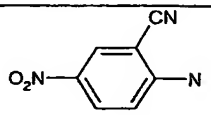
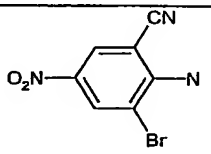
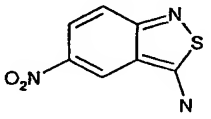
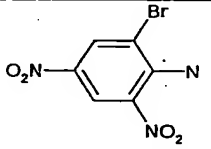
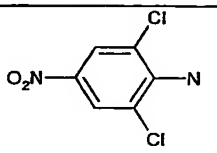
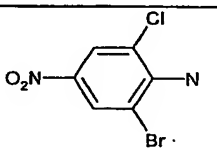
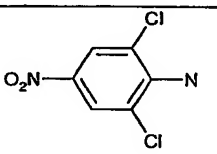
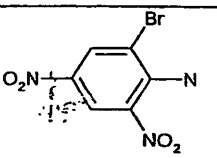
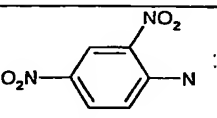


(Ih)

were prepared by the procedure of Example 213 (see Table 11)

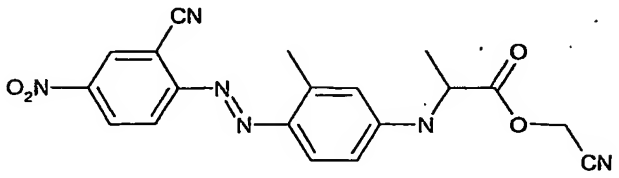
Table 11

Example	D'''''	R^{29}	R^{30}	R^{31}	λmax (nm)
214		-H	$-CH_3$	$-CH_3$	519

Example	D'''''	R^{29}	R^{30}	R^{31}	λmax (nm)
215		$-CH_3$	$-CH_3$	$-CH_3$	504
216		$-CH_3$	$-CH_3$	$-CH_3$	531
217		$-CH_3$	$-CH_3$	$-CH_3$	537
218		$-CH_3$	$-CH_3$	$-CH_3$	597
219		-H	$-CH_3$	$-CH_3$	517
220		-H	$-CH_3$	$-CH_3$	428
221		-H	$-CH_3$	$-CH_3$	428
222		$-CH_3$	$-CH_3$	$-CH_3$	449
223		$-CH_3$	$-CH_3$	$-CH_3$	539
224		$-CH_3$	$-CH_3$	$-CH_3$	524

Example 225

4-(2-cyano-4-nitrophenylazo)-N-ethyl-N-(1-cyanomethoxy carbonylethyl)-m-toluidine



2-cyano-4-nitroaniline (3.1parts) was set stirring at 5°C with a mixture of acetic acid and propionic acid, 86:14 (40parts). Nitrosyl sulphuric acid 40% (6.6parts) was added below 5°C and the mixture was stirred for 30 minutes.

The diazo solution was added gradually to a stirred coupling mixture of N-ethyl, N-(1-cyanomethoxycarbonylethyl)-m-toluidine (4.1parts), methanol (40parts), water (200parts) and sulphamic acid (1part). After two hours the product was isolated by filtration, washed with cold water and dried to yield, 4-(2-cyano-4-nitrophenylazo)-N-ethyl-N-(1-cyanomethoxycarbonylethyl)-m-toluidine (3.9parts) λmax = 510nm (acetone)

When applied to polyester materials from aqueous dispersion, red shades with excellent wet and light fastness properties were seen.